

July 7, 1970

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3,519,419

SUPERPLASTIC NICKEL ALLOYS

Filed June 30, 1966

4 Sheets-Sheet 1

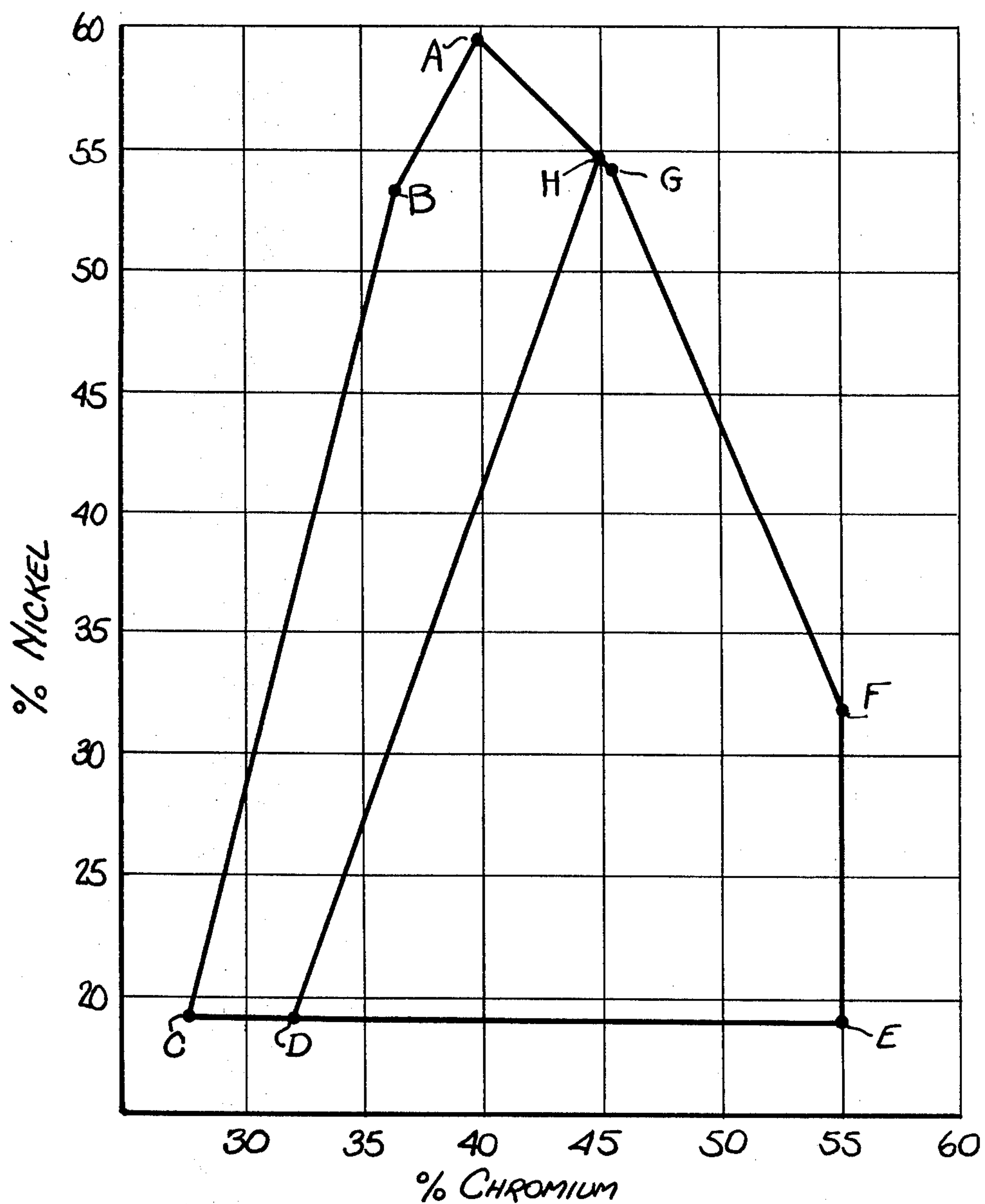


Fig. 1.

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4 Sheets-Sheet 2

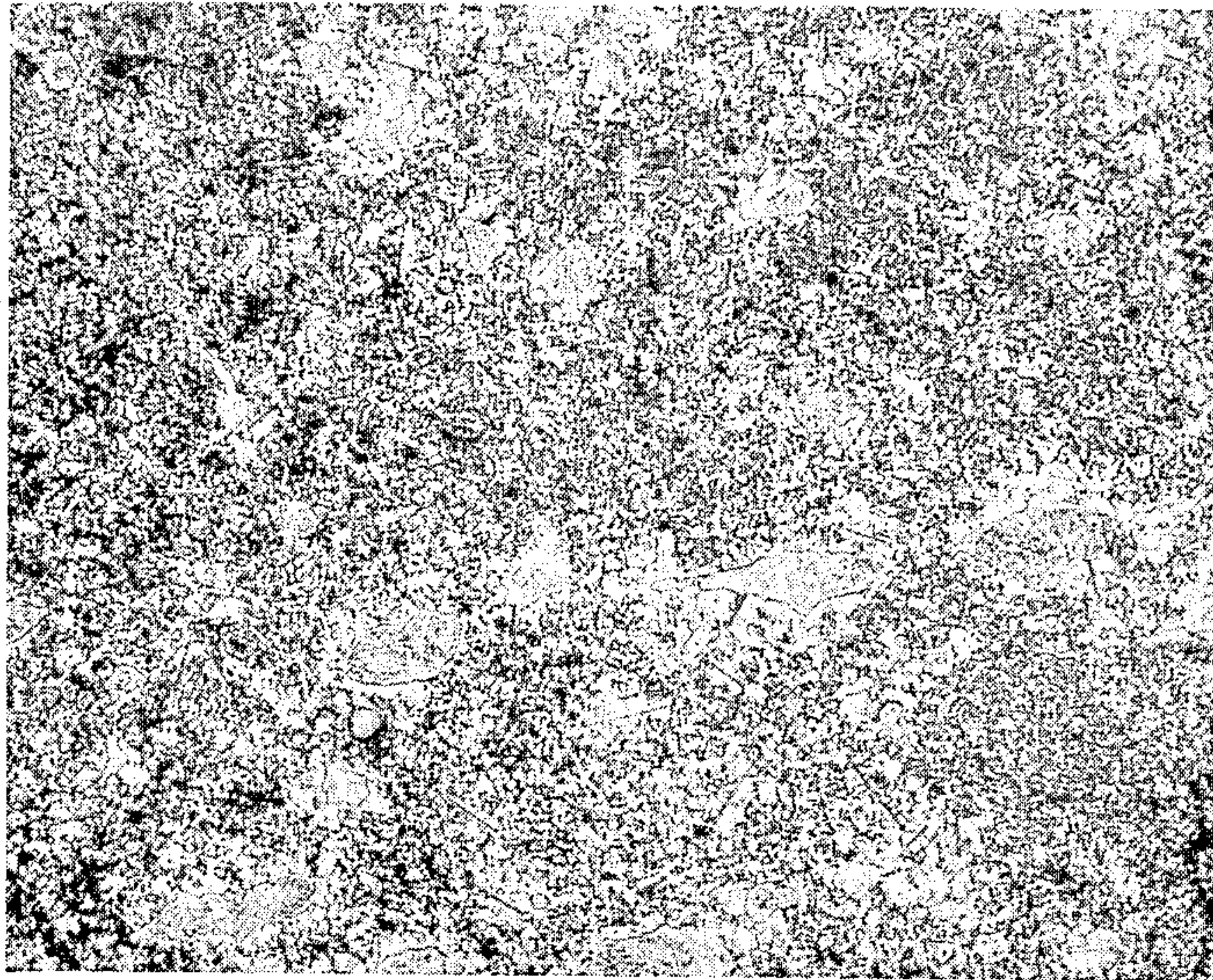


FIG. 2

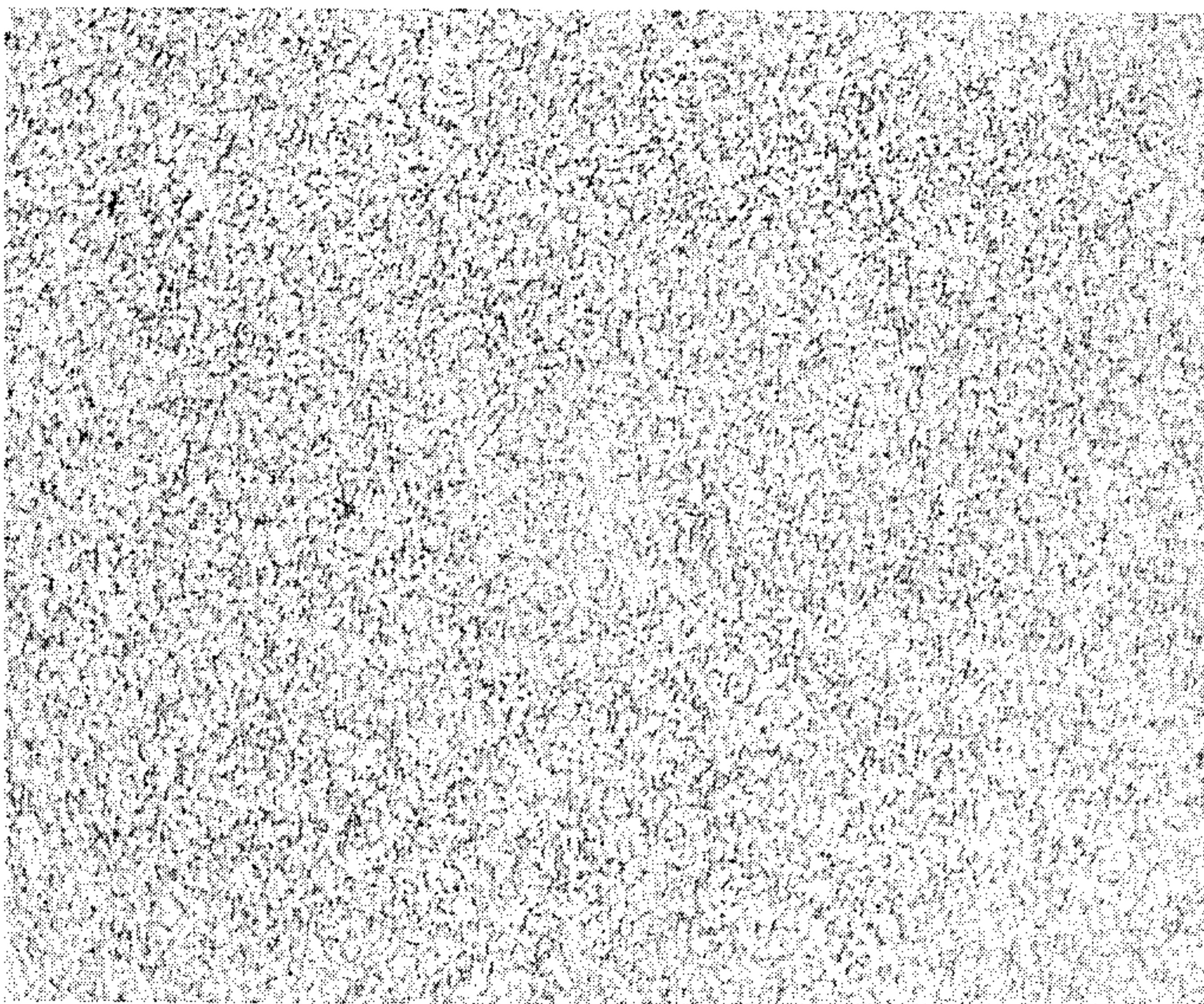


FIG. 3

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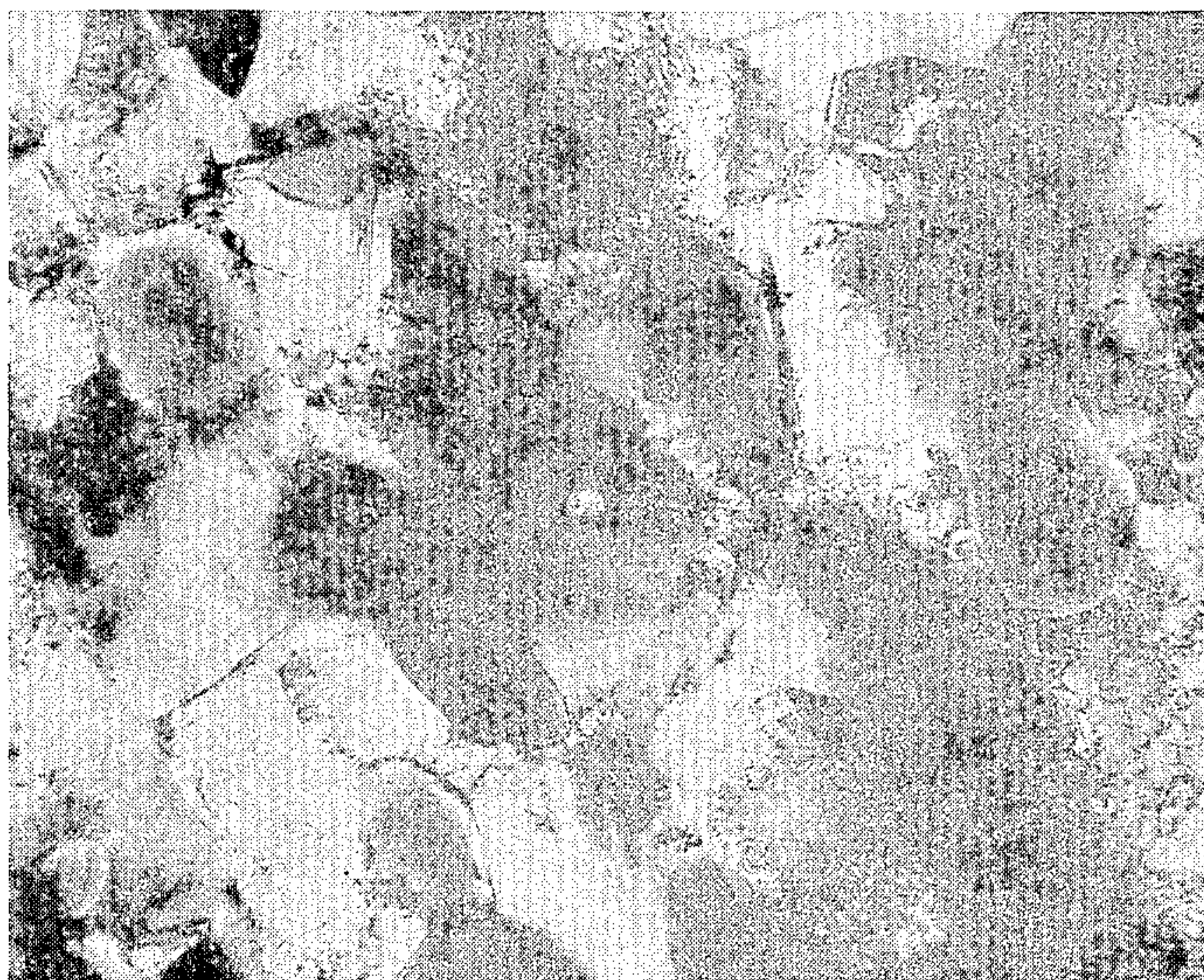


FIG. 4



FIG. 5

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Fig. 6.

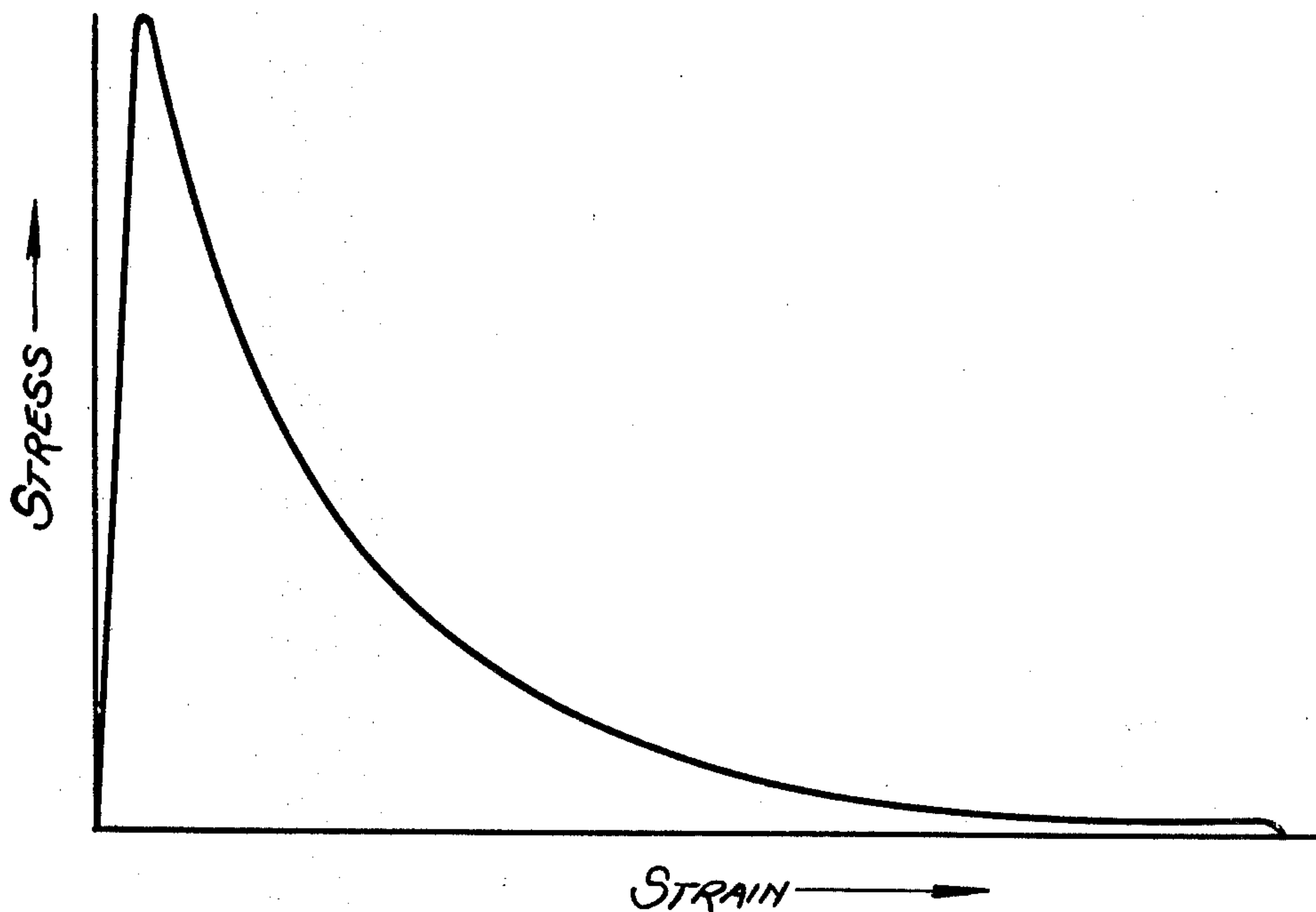
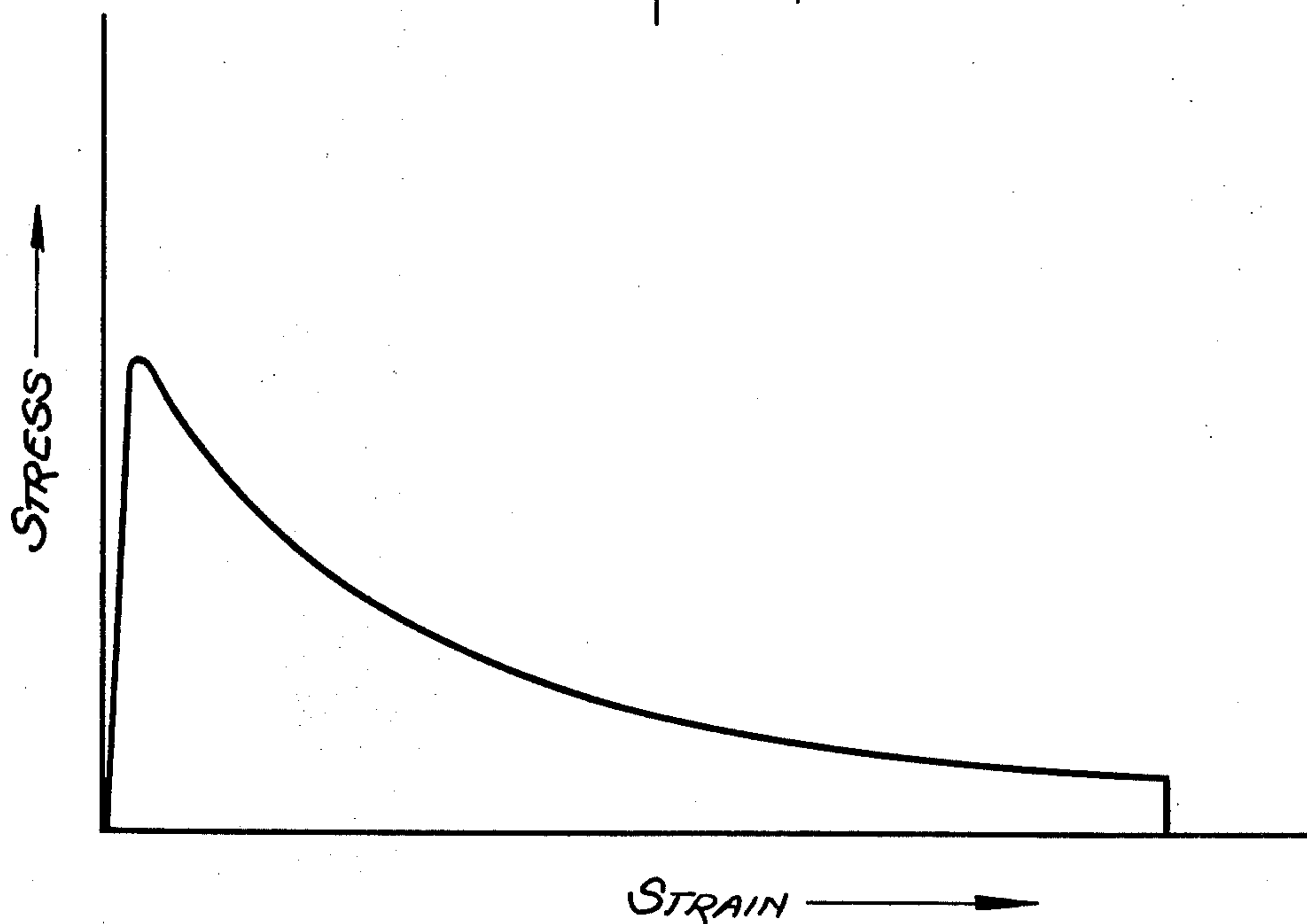


Fig. 7.

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SUPERPLASTIC NICKEL ALLOYS

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U.S. Cl. 75—171

28 Claims

ABSTRACT OF THE DISCLOSURE

Nickel-chromium alloys having fine-grain gamma-alpha phase microstructure and specially controlled composition are characterized by superplastic elongations up to 1000% and greater; thermomechanical processing treatment of certain nickel-chromium alloy compositions produces fine grained gamma-alpha microstructure characterized by superplasticity.

This invention pertains to nickel-chromium alloys, including nickel-chromium-iron alloys, of novel composition, to methods of processing such alloys to impart an unusual microstructure thereto whereby the alloys manifest an extraordinary capability to be hot deformed, e.g., to be tensilely elongated up to 1,000%, and to the so-processed alloys.

As is well known, the excellent mechanical and other properties generally characteristic of nickel-chromium alloys have rendered them eminently suitable for a host of diverse commercial applications. Metallurgical properties, including high room temperature tensile strengths, e.g., on the order of 150,000 pounds per square inch (p.s.i.) and above, good hardness qualities, outstanding resistance to oxidation and to a variety of corrosive media, etc., have significantly contributed to the major role these alloys have assumed in nearly all areas of industrial activity.

Such attributes notwithstanding, prior art nickel-chromium alloys have not, however, been considered as affording exceptionally outstanding hot deformability characteristics. The fact that a great number of such alloys possess high tensile strengths and hardness values, properties which have led to such descriptive terminology as "high temperature alloys," would imply difficulty in hot forming.

Now the present invention is specifically addressed to the broad objective of providing nickel-chromium alloys having markedly enhanced ability to be hot deformed while also having a highly desirable combination of other properties such as high strength at low and intermediate temperatures, hardness, corrosion resistance, etc. It is important commercially to be able to obtain such characteristics in nickel-chromium alloys of high chromium content, of for example, 35% to 50%, in order to take advantage of the enhanced resistance to corrosive environments conferred by such chromium levels, an objective that would, however, appear difficult to achieve in view of the general knowledge that nickel alloys of high chromium content are usually extremely difficult to forge.

In the metallurgical art in general, instances have been reported in which metal specimens have been stretched whereby a portion thereof has been elongated several times its original length. This viscous-like behavior is in marked contrast to most other types of plastic deformation common in metals; for example, conventional tensile and creep deformation where specimens seldom exceed 100% elongation at fracture. However, this superplastic behavior is known mainly as a metallurgical curiosity and has been of little practical value commercially. More-

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over, most instances of superplasticity have been found among alloys of relatively low strengths and low melting points, such as lead-tin and aluminum-zinc alloys, etc., which are, comparatively speaking, extremely pliable inherently. For practical metallurgical purposes, it is important to understand that the unusual characteristics of superplasticity enable elongating alloys high amounts at strain rates which are much higher than the strain rates of metallurgical creep. Although metallurgical creep sometimes results in high elongation, metallurgical creep usually requires many days or even months to effect elongations of 100% or more whereas with superplastic deformation, high elongations of 150% or more can be accomplished in a matter of minutes, e.g., as little as about 7 or 8 minutes. Accordingly, the common kind of deformation by creep is of practically no use for commercial metallurgical production processes and, moreover, the occurrence of high elongation during a creep test does not mean that superplastic deformation has occurred.

Now it has been discovered that the above stated and other desirable objectives, including new superplastic deformability, high room temperature tensile strength and hardness, good corrosion resistance, etc., are obtained with suitably structured nickel-chromium alloys in accordance with the invention containing nickel in an amount of at least 19% and chromium in an amount not greater than 55% with the amounts of nickel and chromium correlated to provide the alloy with chromium in excess of its solubility limit in the alloy matrix, say, by at least 2%, at about 1800° F. Subject to the foregoing, the nickel and chromium contents of the alloy advantageously fall within ranges of about 19% or 20% to about 60.5% and about 24.5% to about 55%, respectively, and the chromium content is related to the nickel content as set forth hereinafter. It is advantageous that the alloy contain iron, particularly in an amount of at least about 7% to promote hot plasticity; however, the iron content should not exceed 55%, e.g., 0.1% to 50% or about 54%. For consistently obtaining superplastic characteristics it has been further found beneficial to include a small amount of a plasticizer in the alloy. A small but effective amount of one or more of the group titanium, magnesium, zirconium, calcium and boron is particularly beneficial as a plasticizer to enhance superplasticity of the alloy when processed as described herein to obtain a special microstructure. Titanium and magnesium in particular are advantageous in obtaining good hot workability for forging or rolling the alloy.

Titanium is by far the most advantageous plasticizer in an amount of about 0.1% to 2.5% and in preferred amounts of about 0.2% or 0.5% to 2% as discussed hereinafter. When the plasticizer is magnesium, zirconium, calcium or boron, the amount thereof can be up to about 0.1% and preferably about 0.001% to 0.05% magnesium, up to about 0.1% and preferably about 0.001% to 0.04% zirconium, up to about 0.05% and preferably about 0.001% to 0.03% calcium, and up to about 0.015%, preferably about 0.001% to 0.012%, boron. For obtaining good forgeability, magnesium is more beneficial than zirconium, calcium or boron, especially at relatively high chromium levels.

The chromium, in addition to not exceeding about 55%, also should not exceed the percentage expressed by the following relationship (whichever is the smaller) in order to assure superplastic deformability of the alloy:

$$(1) \quad \text{Percent Cr} = 68.9 - 0.435 (\text{percent Ni})$$

Further, particularly in respect of the more advantageous alloys, to wit, those containing titanium, the titanium is especially beneficial additionally for obtaining metallurgical integrity during superplastic tensile deformation

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and for obtaining the required microstructure in alloys having relatively low amounts of chromium in relation to nickel. Thus, the minimum percentage of chromium necessary for obtaining the required two phase structure is dependent upon the percentages of both nickel (at least 19%) and any titanium (up to about 2.5%) present. For this purpose, it is especially advantageous that where the alloy contains about 19% to about 53.5% nickel, the chromium in the alloy at least equal the percentage determined by the relationship

$$(2) \text{ Percent Cr} = 0.253(\text{percent Ni}) + 22.9 \\ - K(\text{percent eff. Ti} - 0.36)$$

and where the alloy contains more than 53.5% nickel, e.g., 53.55% to about 59.8% or to about 60.5% nickel, the chromium in the alloy at least equal the percentage determined by the relationship

$$(3) \text{ Percent Cr} = 0.550(\text{percent Ni}) + 7.0 \\ - K(\text{percent eff. Ti} - 0.36)$$

where K is a weighting factor of about 1.5 in both of the foregoing relationship. For assuring a most favorable two phase structure the K factor is about 1.2. The term "percent eff. Ti" refers to the percentage of effective titanium (noncarbide titanium), which is the percent of titanium present in excess of that which combines with any carbon in the alloy, and equals the percent titanium present minus about 4 times the percent carbon, but, of course, is never less than zero. Relationship (2) applies equally to titanium-free alloys, in which instances "percent eff. Ti" is zero.

Proportions of nickel and chromium in certain advantageous embodiments of the invention are illustrated by area ABCEFGA and others on the alloy chart in FIG. 1 of the drawing. Also included in the drawing are reproductions of photomicrographs and electron micrographs, FIGS. 2 through 5, and stress strain plots, FIGS. 6 and 7, relating to alloys of the invention. Referring now to the area ABCEFGA in FIG. 1, the line ABC illustrates advantageous minimum percentages of chromium in relation to nickel in certain of the advantageous alloys containing at least 0.36% effective titanium and line FG in conjunction with line EF at 55% chromium illustrates maximum percentages of chromium in the alloys. For convenience in relating the foregoing relationships to the drawing, it may be noted that nickel-chromium proportion lines through points B and C and through points A and B are represented by relationships (2) and (3), respectively, when the alloys contain 0.36% effective titanium, e.g., 0.6% titanium and 0.06% carbon. Relationship (1) represents a nickel-chromium proportion line through points F and G. Line GA delineates compositions containing about 99.6% nickel plus chromium. The area ABCEFGA in FIG. 1 shows percentages of nickel and chromium in some specially advantageous alloys containing at least 0.36% and up to 2.5% effective titanium. In this area, the chromium content of such alloys is related to the nickel content thereof so as to fall in about the following ranges in accordance with the drawing.

Percent nickel:	Percent chromium
19 -----	27.7 to 55
20 -----	28 to 55
32 -----	31 to 55
53.5 -----	36.5 to 45.6
54.4 -----	36.9 to 45.2
54.7 -----	37.1 to 44.9
59.8 -----	39.8

The chromium contents vary proportionally to nickel for intermediate values in the foregoing tabulation.

In addition to nickel, chromium, titanium or other plasticizing elements and iron, the alloy can also contain up to 0.1%, advantageously 0.005% to 0.08%, carbon and one or more other elements such as, for example, cobalt, aluminum, molybdenum, tungsten, columbium, tantalum, copper, vanadium, silicon, manganese and beryllium in

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percentages as discussed hereinafter. The composition of the alloy can be described in percentage amounts of the various elements with the balance being iron, or nickel, or chromium or a combination of these elements.

When in the superplastic condition and at room temperature the alloy is of an unusually fine, or ultra fine, microstructure comprising gamma and alpha phase constituents based on the nickel-chromium-iron system and is, accordingly, to be understood as being in such an ultra fine structured superplastic condition when referred to herein as the fine grain gamma-alpha alloy of the invention. The gamma phase of the alloy is the face-centered-cubic nickel-chromium solid solution, either with or without iron, and the alpha phase is the body-centered-cubic chromium-rich (e.g., 50% or more of chromium) solid solution containing nickel with or without iron. The fine grain gamma-alpha microstructure has a fine gamma grain matrix and small alpha particles intergranularly dispersed adjacent to the gamma grains. Average grain size of the fine gamma grains is in an ultra fine order of magnitude, usually of about 10 microns or less, and the small alpha particles referred to herein are no larger, and are usually smaller, than 10 microns in average cross section size. Larger alpha particles can also be present in some instances, e.g., when the alloy contains more than about 45% chromium, and do not prevent obtaining superplasticity provided the composition is balanced in accordance with the invention.

One method according to the invention for imparting highly enhanced elevated temperature plasticity to alloys of the present composition comprises heating to a temperature sufficiently high, e.g., 2200° F., to dissolve a substantial portion, and advantageously all, of the more soluble alpha phase to thereby provide at least 2% precipitable alpha-chromium in the alloy, and thereupon hot plastically deforming the alloy, e.g., by extrusion, forging or rolling, refining the gamma phase to an ultra fine grain size and maintaining a fine gamma grain structure while the alloy cools to or through a temperature of alpha precipitation and thereby precipitating fine alpha particles intergranularly adjacent to fine gamma grains to impart to the alloy a fine grain gamma-alpha microstructure having superplastic characteristics. Alternatively after dissolving a substantial portion, and advantageously all, of the alpha phase, the alloy (especially the particularly good cold workable composition referred to hereinafter) can be cold worked to the extent of at least 5% or 10%, and more beneficially at least 30%, reduction in cross sectional area and thereupon heated to a recrystallizing temperature (a temperature at or above the recrystallization temperature, i.e., the minimum recrystallization temperature of the alloy) but not higher than about 1800° F. thereby also to precipitate small alpha particles of ultra fine size and to impart to the alloy the fine grain two-phase gamma-alpha microstructure having superplasticity and other characteristics of high plasticity at elevated temperature. In order to obtain good cold workability the alloy should be annealed, preferably by a solution treatment in the high temperature, substantially all-gamma temperature field, e.g., 2200° F. to 2300° F. or up to just below the incipient melting point of the alloy, followed by a rapid cool or water quench to room temperature to retain all or substantially all the alpha phase in solution. The minimum recrystallization temperature of the cold worked alloy is generally about 1100° F. With either processing the alloys will have imparted thereto a fine structure and, thereby, superplastic characteristics which enable the alloys to be elongated at least about 150% or more, e.g., 800% or 1000%, at high strain rates at 1800° F. The high strain rates at which tensile elongations of 150% and higher are obtained in accordance with the invention are the strain rates existent during constant rate elongation commencing at initial strain rates of at least 0.16 inch per inch per minute (in./in./min.).

The room temperature microstructure of the alloys of the invention depends on the previous history and the

specific composition. When of certain compositions referred to hereinafter and if solution annealed in the gamma temperature field of about 2200° F. and above, and quenched, a substantially all-gamma structure, e.g., not more than 10% undissolved alpha and balance essentially gamma, is attained. Upon reheating to a temperature of about 1100° F. or higher, e.g., 800° F., appropriate for recrystallizing these alloys when cold worked, the quenched gamma phase alloy undergoes a phase transformation without recrystallization of the gamma phase and precipitates alpha phase in the gamma matrix, the microstructure being, however, relatively coarse and not superplastic. On the other hand, if the solution treated and quenched alloy is first cold worked, e.g., cold rolled, at least 5% or 10% and advantageously at least 30%, and is then reheated to a recrystallizing temperature, for example 1100° F. for 16 hours, an ultrafine precipitate of alpha phase particles in a fine grained gamma matrix is obtained with accompanying new and unusual superplastic characteristics. FIG. 2, taken at a magnification of 1000 diameters (1000×), illustrates an etched microstructure of a thus-processed alloy containing 45.1% nickel, 38.3% chromium, 2% titanium, 1% aluminum, 0.06% carbon and the balance essentially iron after the alloy was additionally heated 1 hour at 1800° F. and shows that the fine grain gamma-alpha microstructure was retained within an ultra fine size range during reheating and thus demonstrates that the alloy has good microstructural stability at 1800° F. When elongated at 0.16 inch per minute per inch of initial gage length at 1800° F., the alloy stretched 800% without fracture. In FIG. 2, the very small near-white particles are fine, in fact, ultra fine, alpha and the very dark or black-appearing matter is alpha that is too fine to be resolved at 1000×. The gamma grains lie in the gray areas between the alpha and are known to be of fine average size less than about 3 microns although the grain boundaries thereof could not be resolved by optical microscopy. The relatively large patch-like areas constituting a volumetric proportion of about 7.4% of the illustrated microstructure show alpha (with gamma within) which was not dissolved by previous heat treatment.

Alternatively, if the alloy is slow cooled, without accompanying deformation, to room temperature or even only as low as about 1800° F. to 1600° F. from the gamma temperature field, a relatively coarse gamma-alpha structure is obtained, which again is not productive of superplasticity. If, however, the alloy is heated in the alpha solution temperature field (the gamma temperature field), for example, heated at about 2200° F. to 2300° F. and higher, and is thereupon subjected to a plastic deformation, as by rolling or forging, which is continued with naturally occurring cooling until the temperature drops into the alpha precipitation temperature field, e.g., down through 1800° F. to 1750° F. or 1650° F., an ultra fine precipitate or small alpha particles will occur and a fine grained gamma-alpha microstructure will again be obtained, such as to impart high hot formability as measured by tensile elongations of at least about 150% at high strain rates at 1800° F. FIGS. 3 and 4 (reproductions of a photomicrograph of an etched specimen taken at 1000× and a transmission electron micrograph taken at 28,000×, respectively) illustrate the gamma-alpha microstructure with fine average gamma grain size of about one micron or less resulting from such a hot rolling process performed on alloy 18, having the composition and characteristics referred to in Tables I and II hereinafter. FIG. 5 (a reproduction of a transmission electron micrograph taken at 18,000×) illustrates the microstructure of the same alloy after being superplastically stretched at 1800° F. in accordance with the invention. In FIGS. 4 and 5, solid gray-black particles of alpha are shown adjacent to the boundaries of the lighter shaded gamma grains. Average gamma grain size illustrated by FIG. 5 is of an ultra fine magnitude of 1 to 2 microns.

For obtaining good superplastic formability at, for example, 1700° F. to 1800° F., the microstructure should consist essentially of fine gamma phase grains and chromium-rich alpha phase at least partly occurring as fine particles intergranularly disposed at gamma grain boundaries. In general, the microstructure should comprise about 30% to 98% gamma phase and about 2% to 70% alpha phase, the latter being distributed at least in part substantially at the gamma phase grain boundaries, i.e., intergranularly. (Percentages referred to herein with regard to metallurgical phase are by volume.) For optimum results, at least about 5% of the alpha phase should be present. More beneficially, there is at least 10% alpha in the structure. As to other phases, it might be mentioned that at room temperature the gamma phase in aluminum-containing and titanium-containing alloys herein described may contain gamma prime phase, Ni₃Ti, Al), precipitated in the gamma grains, but any such gamma prime phase is nearly or entirely dissolved when the alloy is heated to 1700° F. or 1800° F. Other phases apart from alpha, gamma, and gamma prime, which may be present in small amounts desirably totalling not more than 2% at room or elevated temperatures include carbide phases, e.g., titanium carbide or chromium carbide, and also eta, laves, carbonitride, etc., phases. Thus, although small amounts of other phases can be present the overall microstructure consists essentially of gamma plus alpha, e.g., at least about 98% gamma plus alpha, at about 1800° F. and higher, and at room temperature consists essentially of gamma plus alpha and optionally gamma prime, e.g., at least 98% gamma plus alpha plus gamma prime.

As indicated hereinbefore, if the desired superplastic hot deformability is to be achieved, the gamma phase grains must be of unusual fineness. The gamma grains must be less than 12 microns and should be on the order of about 10 microns or less and advantageously less than about 3 microns in average size. The fine alpha particles required at grain boundaries desirably should not exceed about 5 microns and highly satisfactory results are achieved with alpha particles of less than about 3 microns. It is not only important to attain a fine grain structure but care must be exercised that it also be maintained. Inappropriate annealing, solution treating or otherwise heat treating at high temperature can promote grain growth or alpha phase solution; for example, prolonged heating of the alloys at temperatures of about 2000° F. and higher induces grain growth and is generally to be avoided unless the alloy is further processed to restore the fine grain gamma-alpha structure as described herein.

At elevated temperatures up to at least about 1800° F., the fine grain gamma-alpha structured alloys possess good metallurgical stability whereby grain size, undissolved alpha phase and also the gamma phase are retained for long periods of time at such temperatures, e.g., 30 minutes to 5 hours at 1600° F. to 1800° F. This microstructural stability is especially required at the highest temperatures and where extended metal forming periods are needed for obtaining large amounts of hot plastic elongation. Any alloys of compositions not in accordance with the invention which may have fine grain two-phase structures only at low temperatures, or during brief transitions or for only short periods at elevated temperatures such as 1800° F. are not satisfactory for achieving superplasticity in accordance with the invention.

It is highly beneficial that at least 0.1% effective titanium be present, even more advantageously 0.35% to 2.3%, not only to obtain optimum plastic deformability but also metallurgical integrity during superplastic working, e.g., in maintaining the alloy in a sound condition without any extensive formation of porosity, fissures, cracks and other voids. When alloys containing, say, about 0.1% to 2.5% effective titanium (as distinguished from the other plasticizers) are superplastically stretched (ex-

tended) sufficiently to cause separation, it occurs without the usual indications of conventional tensile fracture generally associated with fracture initiated by voids generated during tensile stretching. At elevated temperature, titanium-containing alloys in accordance herewith smoothly elongate in a seemingly viscous manner with the formation of very few, if any, voids. Where pulled to separation, cylindrical specimens are reduced in cross section to a sharp point, i.e., reduction in cross sectional area is practically 100%. In contrast, titanium-free alloys, including those to which have been added one or more of the other above-enumerated plasticizers, are appreciably more susceptible to formation of voids and are, therefore, less sound. This is illustrated by the stress strain plots in FIGS. 6 and 7 showing relationships of stress to strain when fine grain gamma-alpha specimens of alloys 31 and 9, having compositions set forth in Table I hereinafter, were superplastically elongated at 1800° F. from an initial strain rate of 0.16 in./in./min. at constant elongation rate. It is evident from the plot in FIG. 6, pertaining to titanium-free alloy 31, which contained a small amount of calcium resulting from adding about 0.05% calcium to the melt, that the stress curve drops abruptly to zero, thereby showing a sudden drop in stress and thus indicating occurrence of void-initiated fracture rather than viscous-like separation. In contrast, FIG. 7 pertaining to titanium-containing alloy 9 (about 0.36% effective titanium) illustrates that the stress for elongating titanium-containing alloys of the invention curves smoothly down to practically zero and elongation can be continued until the cross section is reduced virtually 100%, e.g., 98%. Micrographic examination showed that the titanium-containing alloy remained essentially free from voids while being elongated whereas the other specimen without titanium developed many voids although both had the required superplastic fine grain gamma-alpha microstructure and were of chemical compositions in accordance with the invention.

In consistently achieving a highly satisfactory combination of characteristics, including superplasticity, metallurgical integrity, high ultimate tensile strength, e.g., at least about 130,000 p.s.i., at room temperature, resistance to corrosion, etc., the alloy should contain from about 0.36% to about 2.5% effective titanium with the nickel and chromium being correlated to represent a point falling on the area ABCEFGA of FIG. 1. Further, additional advantages including good cold workability and particularly good isotropic characteristics referred to hereinafter are obtained with alloys containing about 0.36% to 2.5% effective titanium and a nickel-to-chromium relationship satisfying area ABCDHA, which area is illustrative of amounts of nickel and chromium in a compositional field for alloys which can be heated to achieve the substantially all-gamma structure prior to imparting the required fine grain gamma-alpha microstructure.

With regard to other constituents which can be included in the alloys for obtaining special advantages, columbium in amounts up to about 2.5%, e.g., about 0.5% to 2%, is beneficial for improvement of room temperature tensile strength, which is particularly useful in producing wire; copper in amounts up to about 3%, e.g., about 0.5% to 2.5%, affords improved corrosion resistance in marine environments and other dilute chloride media; about 0.05% to 0.4% aluminum is useful for deoxidation purposes but larger amounts up to 1.5%, e.g., about 0.5% to 1%, can be present for conferring precipitation hardening. However, it is important to use no more than the minimum amount of aluminum necessary for a given application, and not more than about 1.5%, since aluminum generally detracts from obtaining the most satisfactory hot plasticity. The total aluminum plus titanium should not exceed about 3.5% and advantageously should not exceed 3% for good hot workability.

The alloys can also contain up to 3% molybdenum and

up to about 1.5% tungsten for enhancing corrosion resistance and room temperature strength, but the total molybdenum plus one half the percentage of tungsten should not exceed about 3% in order to avoid detrimental phases such as the sigma phase and to avoid adversely affecting hot workability. In addition, the alloys can contain up to about 0.1% carbon, up to about 0.5% silicon, up to about 0.5% manganese, up to 4% tantalum, provided the sum of the percent columbium plus one half the percent tantalum in the alloy does not exceed about 2.5% of the alloy, up to about 1% beryllium and up to about 0.2% vanadium. Cobalt in amounts up to 1% or 5% or as much as about 10% can be substituted for equal percentages of nickel, any cobalt present being considered as nickel for purposes of the relationships set forth herein. Commercially the alloys will usually contain some amount of iron, e.g., 0.1% or more iron, although it is to be understood that when ingredients of very high purity are utilized, the alloys can be composed entirely of nickel, chromium and a plasticizer, notably titanium. As plasticizers other than titanium, the alloy can contain up to about 0.1% magnesium, up to about 0.1% zirconium, preferably up to 0.04% zirconium, up to about 0.05% calcium, preferably up to 0.03% calcium and up to about 0.015% boron. Advantageous ranges for magnesium or boron when present in the alloy are about 0.01% to 0.05% and about 0.005% to 0.012%, respectively. Calcium has been effective when retained in only spectrographically discernible amounts and zirconium has been found effective when added as a plasticizer even when any amount finally present in the alloy was not detectable spectrographically. In any event, the total percentage of elements other than nickel, cobalt, chromium, iron and plasticizer should not exceed about 7%. In many advantageous embodiments of the alloy the total of nickel, chromium, iron and plasticizer is at least about 97%.

Subsequent to other desired processing, if any, the super-plastic condition contemplated herein is achieved by precipitating alpha-chromium intergranularly among fine gamma grains while maintaining gamma in the fine grain condition. Advantageously, this fine-grain gamma-alpha structure is accomplished by hot working processing as described hereinbefore. In this connection, the initial hot working temperature should be sufficiently high to provide at least about 2% precipitable alpha-chromium. Generally, hot working is commenced at temperatures of about 2200° F. to about 2300° F. and is advantageously continued while the alloys cool to below about 1800° F., e.g., to 1700° F. or 1600° F., or even lower. By so doing, alpha chromium precipitates as the temperature drops to about 1800° F. and below and, thus, the alloys are worked or otherwise deformed through a temperature of alpha phase precipitation. This markedly contributes to producing an ultra fine two-phase structure.

The invention additionally provides for producing wrought products having essentially fully equiaxed structures and substantially isotropic ductility characteristics, thereby overcoming disadvantages of anisotropic ductility often present in other wrought products made by unidirectionally rolling previously known high strength nickel-chromium alloys. To obtain isotropic advantages in accordance with the invention, the alloy should be substantially all-gamma phase, advantageously consisting practically entirely of gamma, at the beginning of a hot working operation used to impart the fine grain gamma-alpha structure; to accomplish this, special control of the alloy composition is needed. Where the substantially all-gamma condition is required at some stage of processing the alloy, whether for obtaining isotropy, good cold workability or other advantages including particularly good hot workability for forging or rolling, the percentages of chromium and nickel in the alloy should be correlated so as to fall on or to the left (the direction of lower chromium) of line DH in FIG. 1. The chromium-nickel per-

centage line passing through D and H is represented by the following relationship:

(4) percent Cr=0.361(percent Ni)+25.1

Accordingly, alloy compositions for obtaining the substantially all-gamma condition should contain chromium in amounts up to the percentage determined by relationship (4) and, in order to be in accordance with the invention, at least the percentage required for relationships (2) and (3) in correlation to the percentages of nickel and any titanium in the alloys. With the chromium content controlled to be within the range from relationships (2) and (3) up to relationship (4) and, of course, with nickel at least 19%, the alloy is substantially all-gamma and does not contain more than about 10% undissolved alpha when at 2200° F. and higher. In alloys with more chromium than is called for by relationship (4), the amount of alpha therein which is not dissolved at 2200° F., e.g., primary alpha, increases with increase in the chromium content and is usually in the form of relatively large coarse particles. Although very good superplastic characteristics can be obtained when undissolved alpha is present in the alloy at the commencement of hot working, alpha phase, if initially present in large amounts, tends to become elongated into stringers during hot working and such stringers when present in wrought products interfere with obtaining isotropic characteristics. Particularly satisfactory superplastic alloys characterized by isotropy are obtained by heating alloys having specially controlled compositions with chromium from percentages in accordance with relationships (2) and (3) up to percentages in accordance with relationship (4) to a temperature of about 2200° F. to about 2300° F. and thereafter continuously working the alloy from such a temperature to reduce the cross sectional area thereof about 30% or more and to refine the average gamma grain size to about 10 microns or less cooling down to at least 1750° F. but not below temperatures of rapid recrystallization, e.g., not below about 1600° F. Control of the composition in the aforescribed manner to provide that the alloy be substantially all-gamma at 2200° F. and incorporation of at least 7% iron in the alloy is also recommended in the event that it is desired to hot forge or hot roll the alloy without titanium or magnesium. Extursion may be required in order to accomplish the hot working, at least in the early stages, of low-iron or iron-free alloys of the invention, or those containing chromium in excess of the amount required for relationship (4), if titanium or magnesium are not used as a plasticizer in the alloy.

All alloys of composition and microstructure in accordance herewith possess new and unusual superplastic characteristics enabling the alloys to be plastically deformed in tension at about 1800° F. at high strain rates at least equivalent to constant tensile elongation rate commencing at an initial strain rate of about 0.16 in./in./min.; and by this process deformations equivalent to tensile elongations of over 150%, e.g., 400% or 800%, can be successfully accomplished without cracking or fracturing. Under such conditions of superplastic deformation, the alloys of the invention are generally characterized by unusual strain rate sensitivity, e.g., a strain rate exponent of about 0.5 at 1800° F. at strain rates from about 0.16 in./in./min. to about 1.6 in./in./min. or even 4 in./in./min. As a result thereof, low resistance to deformation during hot working ensues by maintaining the strain rate not greater than 5 in./in./min., preferably not greater than 3 in./in./min. Although the resistance to deformation is greater at somewhat higher strain rates, such as 30 in./in./min. to 90 in./in./min., the alloys nonetheless manifest good hot workability over a wide range of strain rate and can be hot rolled, for example, at mill speeds of about 50 feet per minute to 150 feet per minute (ft./min.), at temperatures of about 1700° F. to 2200° F. with relatively low rolling force.

Where the alloys contain at least about 1% titanium and/or aluminum, room temperature tensile strength can be increased by a hardening treatment comprising heating at about 1050° F. to 1500° F., advantageously 1100° F. to 1200° F., for about ½ hour to about 24 hours. It is of special note that such strengthening can be obtained with little or no degradation of ductility. For obtaining ductility in combination with high hardness and especially high strength of at least 200,000 pounds per square inch (p.s.i.) ultimate tensile strength at room temperature in the age hardened condition, the age hardenable alloys should contain 1% to about 2% titanium, about 0.5% to 1.5% aluminum, with the sum of titanium plus aluminum being about 2.5% to about 3.5%, at least about 19% nickel, chromium in amounts up to 55% and at least in accordance with relationships (2) and (3) and not greater than determined by relationship (1) with the balance essentially iron in an amount not exceeding 30% of the alloy.

The following test data exemplify the hot formability obtainable with fine grained wrought alloys according to the invention.

Chemical compositions of examples of the superplastic alloys of the invention are set forth in Table I. The alloys were vacuum melted and cast into ingots and thereafter were hot worked down through (and thus below) the temperature range of about 2200° F. to 1800° F. to reduce the cross sectional areas of the ingots at least about 75% and to provide fine grain gamma-alpha phase alloys in accordance with the invention.

Results set forth in Table II show the percentage elongations and other properties which were exhibited at 1800° F. by stretching specimens of the fine grained gamma-alpha alloys at that temperature at a constant elongation rate from an initial strain rate of 0.16 in./in./min.

TABLE I

Alloy No.	Percent						
	Ni	Cr	Fe	Ti	Al	C	Other
1-----	23.1	43.0	(33.22)	0.63	-----	0.05	
2-----	35.4	50.0	(13.95)	0.60	-----	0.05	
3-----	26.0	48.0	(25.35)	0.60	-----	0.05	
4-----	(55.5)	43.8	-----	0.63	-----	0.05	
5-----	(47.3)	40.8	9.8	1.05	0.95	0.059	
6-----	(48.3)	39.2	9.7	2.15	0.63	0.022	
7-----	(48)	39.0	9.8	2.12	1.03	0.046	
8-----	(48.3)	39.2	10.1	1.07	1.27	0.049	
9-----	(45.2)	39.2	15.0	0.57	-----	0.060	
10-----	27.5	38.5	(33.33)	0.62	-----	0.05	
11-----	20.0	38.0	(41.4)	0.62	-----	0.05	
12-----	(50.0)	37.6	8.7	1.87	1.05	0.03	
13-----	51	39	(10)	-----	-----	0.06	
14-----	(31.1)	37.2	31.0	0.60	-----	0.056	
15-----	(48.2)	39	10	1.75	1	0.008	
16-----	43	38.5	(18.5)	-----	-----	0.06	
17-----	(51.5)	34.8	10.3	2.04	1.33	0.04	
18-----	(50)	39	8	2	1	0.06	
19-----	(54.2)	33.3	10	2.5	0.05	0.005	
20-----	(52.2)	34.0	10.5	2.10	1.11	0.043	
21-----	38.5	33.4	(32.4)	0.64	-----	0.035	
22-----	44.2	33.2	(22)	0.58	-----	0.005	
23-----	36.2	32.2	(30.9)	0.68	-----	0.058	
24-----	(52.2)	35.4	10.5	1.02	0.86	0.045	
25-----	(34.8)	30.7	32	2.5	0.05	0.022	
26-----	(20.3)	28.0	51.0	0.60	-----	0.065	
27-----	(19.4)	28	52.0	0.59	-----	0.056	
28-----	(20.8)	26.7	50	2.5	0.05	0.021	
29-----	(58.9)	40.5	-----	0.57	-----	0.033	
30-----	(50)	39	10	-----	-----	0.06	1 Cb;
31-----	(48)	42	10	-----	0.05	0.06	Ca added and present <0.02%.
32-----	(48)	42	10	-----	0.05	0.06	0.02 Mg.
33-----	(48)	42	10	-----	0.05	0.06	0.012 B.
34-----	(48)	42	10	-----	0.05	0.06	0.04% Zr added.
35-----	(25)	38	37	-----	0.05	0.06	0.04 Mg.

NOTE.—Figures in parentheses denote balance.

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TABLE II

Alloy No.	Elongation, percent	Ultimate tensile strength, p.s.i.
1.....	>1,000	8,200
2.....	400	13,700
3.....	480	10,100
4.....	720	4,500
5.....	400	8,280
6.....	980	4,520
7.....	580	6,120
8.....	360	7,080
9.....	740	5,400
10.....	520	9,500
11.....	160	20,700
12.....	>860	5,200
13.....	177	9,700
14.....	>740	7,400
15.....	>880	3,800
16.....	416	6,100
17.....	540	6,760
18.....	>1,000	2,700
19.....	220	10,400
20.....	620	9,480
21.....	180	12,100
22.....	180	13,400
23.....	160	13,360
24.....	160	14,600
25.....	290	8,300
26.....	160	14,200
27.....	260	11,900
28.....	388	8,980
29.....	160	13,200
30.....	176	13,700
31.....	504	4,200
32.....	>895	5,400
33.....	508	6,000
34.....	670	6,600
35.....	780	9,400

NOTE.—Elongations were obtained with 1.25-inch gauge length and an elongation rate of 0.2-inch per minute. Results denoted by > pertain to specimens which did not fracture.

It is to be noted that rather phenomenal superplastic characteristics are reported in Table II. Each alloy manifested an elongation over 150% at 1800° F. without fracture. A number of the alloys, e.g., alloys 1, 6, 7, 9, 12 and 18, exemplify an especially advantageous nickel-chromium alloy composition containing 34% to about 43% chromium in an amount at least sufficient to satisfy relationships (2) and (3), about 7% to about 34% iron, about 0.55% to 2.2% or 2.5% titanium, up to about 0.08% carbon, up to about 1.4% aluminum, with at least about 0.36% effective titanium and a titanium-to-aluminum ratio of at least about 1.5:1 and balance essentially nickel, e.g., about 23% to about 53% or 55% nickel, and consistently characterized by very high superplastic elongation of at least about 500% at 1800° F.

In those instances where rupture occurred in specimens of titanium-containing alloys referred to in Tables I and II, the specimens separated with sharp points and exhibited reductions in area of at least about 98%. Specimens without titanium exhibited abrupt fractures and lower reductions in area, e.g., reduction in area for alloy 31 was 89% and alloys 33, 34 and 35 each fractured with only 92% reduction in area.

Superplastic elongations obtained with specimens of alloy 12 at temperatures ranging from 1600° F. to 2000° F. at constant elongation rates starting at two different strain rates are shown by the test results set forth in Table III.

TABLE III

Temperature, ° F.:	Elongation, percent	
	Initial strain rate, 0.16 in./in./min.	Initial strain rate, 1.6 in./in./min.
1,600.....	440	360
1,750.....	420	460
1,800.....	>860	480
1,850.....	500	500
1,900.....	520	290
2,000.....	480	380

The capability of the alloys to be elongated superplastically over a wide range of strain rates including strain rates initially as high as 16 in./in./min. is further confirmed by the results given in Table IV obtained in test-

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ing alloy 40 (of composition in Table VII hereinafter) at 1800° F. Ultimate tensile strength values are included to illustrate strain rate effects on this characteristic.

TABLE IV

	U.T.S. (p.s.i.)	Elongation, percent
Initial strain rate (in./in./min.):		
0.16.....	2,700	960
0.4.....	6,500	960
0.8.....	9,300	880
1.6.....	10,600	1,000
4.....	16,500	920
8.....	18,900	540
12.....	21,200	420
16.....	22,100	480

Additional results from tests of alloy 15 in the fine grain gamma-alpha condition, which demonstrate superplastic characteristics obtained in accordance with the invention at high elongation rates from 0.16 in./min. to 0.8 in./min. and up to 16 in./min. per inch of gage length at temperatures from 1500° F. to 1800° F., are set forth in Table V.

TABLE V

	Initial strain rate (in./in./min.)	U.T.S. (p.s.i.)	Elongation, percent
Temperature ° F.:			
30	1,800.....	0.16	3,800
		0.40	6,000
		0.80	8,700
		1.6	13,000
		4.0	19,000
		8.0	24,500
35	1,700.....	16.0	29,500
		0.16	5,000
		0.40	8,000
		0.80	11,200
		1.6	15,800
		4.0	24,000
40	1,600.....	8.0	28,500
		16.0	36,800
		0.16	8,300
		0.40	12,700
		0.80	17,400
		1.6	23,000
45	1,500.....	4.0	33,500
		8.0	39,000
		16.0	45,000
		0.16	15,500
		0.4	26,000
		0.8	29,500

It should be particularly noted that the high elongation rates at which the results in Tables II through V were obtained are at least several times greater than usual standard short-time tensile test strain rates, e.g., 0.005 in./in./min. to 0.05 in./in./min., and thus not to be confused with results obtained by standard short-time tensile testing.

The following series of examples illustrates obtaining superplastic characteristics in accordance with the invention through cold-work processing and also through hot-work processing of different portions of a specific embodiment (alloy 36) of the invention. Alloy 36, which contained about 47.6% nickel, 38.0% chromium, 2.04% titanium, 0.64% aluminum, 0.01% carbon and balance iron, was hot worked at temperatures from 2200° F. down to 1800° F. into 3/4" diameter bar stock having the fine grain gamma-alpha structure of the invention, thereby providing hot worked alloy 36A. A portion of alloy 36A was solution annealed, with cooling by water quenching, thus destroying the fine grain gamma-alpha structure and providing a solution annealed alloy having a coarse grain substantially all-gamma microstructure which is not superplastic. The annealed alloy was then cold worked to 50% reduction in cross sectional area. A portion of the thus cold worked alloy, which was still in a substantially all-gamma condition, was aged 16 hours at 1100° F. to recrystallize the alloy into an ultrafine structure and to precipitate fine alpha particles intergranularly therein, thereby providing fine grain gamma-alpha alloy 36B in accordance with the invention. Alloy 36B was heated to 1800° F. for superplastic elongation at 0.16 in./in./min.

initial strain rate and a very high elongation of 800% without rupture was obtained. Another portion of the cold worked alloy from which alloy 36B was obtained was heated to 1800° F. for superplastic elongation. In this manner, the cold worked alloy was again recrystallized with accompanying precipitation of alpha particles and thereby converted to fine grain gamma-alpha alloy 36C, also in accordance with the invention, by the usual heating to 1800° F. for superplastic elongation referred to herein, which treatment consisted of heating from room temperature to 1800° F. in about ½ hour and holding at 1800° F. for about 20 minutes prior to pulling. Elongation of alloy 36C at 0.16 in./in./min. initial strain rate at 1800° F. was about 400% prior to rupture separation of this specimen. A specimen of alloy 36A in the hot worked condition was also pulled at 1800° F. and 0.16 in./in./min. initial strain rate and a very high elongation of 800% without rupture was obtained. These results obtained in testing alloys 36A, 36B and 36C illustrate that very good superplastic characteristics are obtained either in the hot-worked condition without cold work or in the annealed-plus-cold worked condition of the new alloy, that recrystallization and precipitation heat treatments over a range of temperatures from 1100° F. to 1800° F. are satisfactory for obtaining the fine grain gamma-alpha condition in cold worked alloys of the invention and that for heat treating cold worked alloys an aging treatment such as ½ hour to 24 hours at about 1100° F. to about 1200° F., e.g., the aging treatment applied to alloy 36B, provides very substantially enhanced superplastic deformability in comparison with results obtained by heating cold worked alloys to 1800° F. in a rather short time and holding for a short period at 1800° F., e.g., the aforementioned heating of alloy 36C for elongation at 1800° F.

It is to be emphasized that the fine grain structured alloys of the invention have superplastic characteristics which greatly differ in kind from other types of plastic deformation characteristics common to alloys having coarse grain structures including even those of the same chemical composition contemplated herein. By way of illustration, three fine grain alloys in accordance herewith and nominally containing 50% nickel, 39% chromium, 2% titanium, 1% aluminum and balance iron had fine gamma-alpha structures with gamma grain sizes of 9, 4.6 and 2.5 microns, respectively, and were characterized by superplastic deformability with elongations at 1800° F. of 220%, 440% and over 1000%, respectively. In contrast thereto, other alloys of the same composition but which had coarse grain structures with gamma grain sizes of 27 microns and 231 microns were found to be, under the same conditions of test, of conventional ductility with elongations of only 80% and 40%, respectively. The fine grain structure contemplated herein, which is of ultra fine size, will be easily distinguishable by those skilled in the art from the coarse grain structures of conventional alloys notwithstanding such coarse grain structures, e.g., 20 microns average cross section, may be sufficiently fine, by conventional standards, to be elsewhere commonly termed "fine grain." For quantitative purposes, the gamma grain size referred to herein is determined from the formula.

Gamma grain size= $3/2 (1/N_{LGB})$ microns where $(1/N_{LGB})$ is an average intragranular dimension, in microns per grain, obtained by averaging the intragranular distances between a representative number of gamma grain boundaries intersecting one or more randomly oriented lines on a micrograph. While a 10-micron grain size microstructure of an alloy of the invention can be differentiated by optical microscopy from other alloys having larger grain sizes, the very fine grain sizes of 5 microns and less, often present in the alloy of the invention, are so fine as not to be easily resolvable by optical microscopy. Electron micrographs are usually needed if such very fine grain sizes are to be accurately measured. An example of a fine grain gamma-alpha

microstructure having an average grain size of about 1 to 2 microns in accordance with the invention is illustrated by FIG. 5.

That room temperature tensile characteristics of the fine grain, wrought alloys within the invention are substantially isotropic when unidirectionally rolled is illustrated by the data in Table VI hereinafter, as is also the importance of maintaining the fine grain two-phase condition. In Table VI each of alloys 37, 37Z and 37Y nominally contained about 48% nickel, 39% chromium, 2% titanium, 1% aluminum with the balance iron, and was forged from 2200° F. down through 1800° F. to provide the fine grain gamma-alpha phase structure. Alloy 37 was unidirectionally hot rolled at about 1800° F. with the fine grain gamma-alpha structure being maintained. Alloy 37Z after being forged was annealed for ½ hour at 2200° F., thereby coarsening the grain structure and partially dissolving the alpha phase, quickly cooled to room temperature, and then reheated to 1800° F. and unidirectionally rolled at 1800° F. Alloy 37Y after being forged was heated to and unidirectionally rolled at about 2050° F., which treatment destroyed the fine grain structure. Elongation and reduction in area values of alloys 37Z and 37Y reflect that anisotropy—not isotropy—resulted. It is also to be noted that the yield strength resulting from rolling alloy 37Y at 2050° F. was appreciably lower than the yield strength obtained from rolling of alloy 37 at 1800° F. (The aged conditions referred to in Table VI were obtained by heating the unidirectionally rolled alloy for 16 hours at the indicated temperatures followed by air cooling).

TABLE VI

Alloy No.	Condition	Test direction	U.T.S., k.s.i.	Y.S., k.s.i.	Elongation, percent	R.A., percent
37	As-rolled	L	204.6	165.7	18	34
		T	207.0	172.3	18	33
	1100° F. age	L	210.9	184.5	16	32
		T	210.9	184.6	18	33
37Z	As-rolled	L	204.4	167.1	20	40
		T	202.4	169.5	18	20
	1100° F. age	L	208.7	181.9	21	39
		T	206.4	183.2	15	20
37Y	As-rolled	L	193.9	136.3	22	38
		T	186.1	135.6	9	14
	1200° F. age	L	195.0	149.8	20	32
		T	194.3	147.6	14	16

Notes:
L=Longitudinal (specimen taken parallel to direction of rolling).
T=Transverse (specimen taken transverse to direction of rolling).
U.T.S., k.s.i.=Ultimate tensile strength in units of 1,000 pounds per square inch.
Y.S., k.s.i.=Yield strength, at 0.2% offset, in units of 1,000 pounds per square inch.
Elongation, percent=Percent elongation in 1.25 inches.
R.A., percent=Percent reduction in area.

Room temperature characteristics of the new alloys contemplated herein are further illustrated by the tensile properties reported in Table VIII for alloys 38 through 47, the compositions of which are given in Table VII. Alloys 38 through 45 were vacuum melted, 46 and 47 being air melted. All were hot worked from about 2300° F. to 2200° F. down through 1800° F. and produced in the fine grain gamma-alpha condition. Alloys 38 through 42 represent hot rolling forged 2" square section billets to ⅝" round bars at temperatures from 2200° F. through 1800° F. and further down to around 1550° F. or 1500° F. Thus, after being hot worked (H.W.) to the fine-grain gamma-alpha condition, these alloys were subjected to substantial amounts of warm working (W.W.) following the hot working operation without interruption. Hot rolling of alloys 43 through 47 was finished at somewhat higher temperatures and thus had relatively little or no warm working. Aging treatments were in the range of

16 hours to 20 hours at the temperatures indicated in Table VIII.

TABLE VII
Percent

Alloy No.	Ni	Cr	Fe	Ti	Al	C	Other
38.....	(56)	38.8	2.15	2.02	0.98	0.07	
39.....	(55.9)	37.3	3.5	2.05	1.05	0.07	
40.....	(47.5)	40.0	9.4	2	1	0.06	
41.....	(44.8)	38.9	13.4	1.91	0.98	0.05	
42.....	(48.6)	39.0	9.09	1.80	1.04	0.05	0.50 Cb.
43.....	48.9	38.9	(8.7)	1.73	0.87	0.003	
44.....	48.5	40	(8.5)	2	1	0.01	
45.....	51.5	45		1	0.5	0.05	2 Cb.
46.....	(47.8)	39	(10)	1.75	1	0.08	0.5 Cb.
47.....	(53.7)	38.1	12.7	0.25	0.88	0.09	1.83 Cb.

NOTE.—Figures in parenthesis denote balance.

TABLE VIII

Alloy No.	Condition	U.T.S., (k.s.i.)	Y.S., k.s.i.	Elongation, percent	R.A., percent
38.....	H.W. plus W.W.	266.5	252.5	6	26
	H.W. plus W.W. plus 1200° F. age	284.6	279.5	6	24
39.....	H.W. plus W.W.	273.6	256.5	5	18
	H.W. plus W.W. plus 1200° F. age	289.9	277.8	6	24
40.....	H.W. plus W.W.	275.3	259.1	4	16
	H.W. plus W.W. plus 1200° F. age	270.7	264.7	6	22
41.....	H.W. plus W.W.	267.2	248.0	5	16
	H.W. plus W.W. plus 1200° F. age	271.3	261.2	5	28
42.....	N.W. plus W.W.	259.1	242.9	6	22
	N.W. plus W.W. plus 1200° F. age	265.7	261.7	7	22
43.....	H.W.	230.4	208.4	6	13
44.....	H.W.	243.3	219.5	7	19
	H.W. plus 1300° F. age	239.6	229.8	5	27
45.....	H.W.	228.0	207.5	10	32
	H.W. plus 1300° F. age	230.7	213.5	3	11
46.....	H.W.	232.4	212.4	7	20
	H.W. plus 1200° F. age	252.1	243.9	4	12
47.....	H.W.	197.4	178.6	10	28
	H.W. plus 1200° F. age	237.5	211.6	4	6

Of special note in Table VIII, alloys 38 through 42 illustrate particularly advantageous combinations of room temperature characteristics, including high yield strengths of 250,000 p.s.i. and higher, e.g., 275,000 p.s.i., coupled with good ductility which are obtained with wrought alloys in the warm worked and aged condition. At room temperature the alloys have an unusually high elastic modulus of about 32,000,000 p.s.i. Alloys in the hot worked-warm worked condition were characterized by advantageously high room temperature strength in addition to superplastic elevated temperature characteristics which are also possessed by alloys 43 to 47. Although the highest room temperature strength is not always obtained by finishing within the range of rapid recrystallization temperatures, such practice is advantageous from the viewpoint of obtaining isotropic characteristics. Air melted alloys 46 and 47 contain columbium in amounts of about 0.5% to about 1.8% which was effective for obtaining cleaner melts under air, that is, less scum, entrapped oxides, etc., than would be achieved in the absence of columbium.

Tensile strength at room temperature in excess of 300,000 p.s.i. and hardness levels as high as Rc 59 have been obtained with cold worked and age hardened alloys. For example, a wrought alloy nominally containing 46% nickel, 39% chromium, 2% titanium, 1% aluminum, 0.06% carbon with the balance iron, was solution treated at 2200° F., cold worked to 30% reduction in thickness and then aged 16 hours at 1100° F. As treated, the fine grain gamma-alpha alloy had a room temperature ultimate tensile strength of 322,000 p.s.i. and a yield strength of 308,800 p.s.i.

To contrast the marked advantages of the invention, a number of alloys outside the scope of the subject invention, alloys A through H, are set forth in Table IX. Tensile elongations of alloys A and C through G when pulled to fracture at 1800° F. from an initial strain rate of 0.16 in./in./min. after hot working from about 2200° F.

down through 1800° F. to accomplish cross-sectional reductions of about 75% or more are also set forth. Alloy B was pulled to fracture at 1825° F. from an initial strain rate of 0.04 in./in./min. after similar hot working.

TABLE IX

Alloy:	Percent						Elongation
	Ni	Cr	Fe	Ti	Al	C	
A.....	(49.9)	49.5		0.60		0.05	101
B.....	(60.0)	40.0					00
C.....	45.0	50.0	(4.4)	0.60		0.05	120
D.....	31.4	29	(39)	0.6		0.05	120
E.....	32	29	(38.9)		0.05	0.06	04
F ¹	(59.5)	34.1		0.86	1.03	0.007	60
G.....	24.5	23	(50)		2.5	0.026	186
H.....	15.4	41.0	(42.9)	0.64		0.05	

¹ Contained 4% Mo and 0.56% Ta.

NOTE.—Figures in parentheses denote balance.

It is to be particularly noted that alloys A through G fractured at values well below 150% elongation and thus failed to exhibit the superplastic tensile workability of the invention. Alloy H contained a large proportion of sigma phase and was extremely hard and brittle, so much so that a test specimen thereof could not be machined by the methods employed for making the other specimens.

Alloys in accordance herewith are characterized by generally high corrosion resistance including resistance to pitting and crevice corrosion in marine environments and other dilute aqueous halide solutions, to general corrosion in high purity water, etc. For example, tests of an alloy containing 46.5% nickel, 39% chromium, 2% titanium, 1% aluminum, 1.5% copper and the balance iron in a 10% ferric chloride aqueous solution indicated that resistance to pitting and crevice corrosion in salt water and other dilute solutions is substantially superior to that of the AISI 300 series stainless steels. Alloy 37 showed good stress-corrosion resistance with a double U-bend specimen. The alloy did not crack during eight weeks submersion in high purity water at 600° F. in an autoclave.

For obtaining advantageously high resistance to corrosion by sulfur and/or lead compounds at elevated temperatures, alloys 1, 3, 9, 10 and 12 of Table I were found especially suitable. When tested for resistance to lead sulfidation by immersion in a molten mixture of lead sulfate, lead oxide and lead chloride at 1700° F., fine grain gamma-alpha phase alloys 1, 3, 9, 10 and 12 underwent only about one-half the percent weight loss suffered by specimens of each of two other alloys, one of which was alloy D of Table IX and the second of which was a binary alloy containing 40% chromium and balance nickel, a composition which is not in accordance with the invention. For obtaining high corrosion resistance in such media over extended periods of time, it is additionally advantageous to restrict the iron content of the alloy to about 20% or less.

The fine grain gamma-alpha structure of the alloys of the invention contributes importantly to corrosion resistance. It has been found that such alloys are substantially more resistant to lead sulfidation than alloys of essentially the same composition but with coarse grains and less precipitated alpha. The corrosion weight loss of an alloy otherwise within the invention but which had been annealed so as to coarsen the grain structure and dissolve much of the alpha phase had a corrosion weight loss about 1.6 times as great as the weight loss of a fine grain alloy of the same composition within the invention when both were immersed in a mixture of molten lead compounds.

A particularly noteworthy advantage is that the alloys of the invention having the wrought, fine grained gamma-alpha structure, can be hot rolled at relatively low rolling loads similar to those encountered in hot rolling many other nickel-chromium alloys of much lower chromium contents and/or much lower obtainable strengths at room

temperature. This is reflected by the data set forth in Tables X and XI comprising the wrought, fine grained aforementioned alloy 37 containing 39% chromium and two commercially available alloys J and K (both outside the invention). Alloy J contained about 76% nickel, 15.8% chromium, 0.04% carbon with the balance iron and alloy K contained about 18.9% chromium, 11.3% cobalt, 10% molybdenum, 3.1% titanium, 1.5% aluminum, 1.7% iron, 0.1% carbon, 0.007% boron with the balance being nickel. In Table X, room temperature properties of aged alloy 37 (see Table VI) are compared with typical room temperature characteristics of alloys J and K when in commercially provided conditions, to wit, alloy J—hot finished and alloy K—annealed and age hardened. It will be noted that at room temperature substantially more strength is obtainable with alloy 37 than with alloys J and K. From Table XI, which shows rolling loads for hot rolling plate of these three alloys at a variety of temperatures and mill speeds, it is evident that alloy 37 of the invention has the important advantage of being hot workable with low rolling loads which are similar to the rolling loads for alloy J and which are very substantially lower than the loads for rolling alloy K, both of which are much lower in chromium.

TABLE X

	U.T.S. (k.s.i.)	Y.S. (k.s.i.)	Elongation, (percent)
Alloy:			
37-----	210.9	184.5	16
J-----	85-120	35-90	50-30
K-----	160	120	18

TABLE XI

Rolling temperature, ° F.:	Mill speed, ft./min.	Roll separating force for 50% reduction in a single pass, 1,000 lbs./in. width of plate		
		Alloy 37	Alloy J	Alloy K
2200-----	100	95	95	166
	150	100	95	190
2000-----	100	138	125	220
	150	148	138	240
1900-----	100	165	130	-----
	150	168	145	298

Although the higher rolling temperatures referred to in Table XI are conducive to detrimental grain growth and solution of the alpha phase in the fine grain gamma-alpha alloy, alloy 37 was apparently not held at rolling temperature long enough to fully anneal the alloy prior to rolling and, thus, hot workability benefits were obtained from the initially fine grain structure of the alloy. Additional test results showed that among alloys of the same composition, substantially higher roll loads were required for hot rolling annealed, and thus grain coarsened, alloys than were required for hot rolling the fine grain alloy of the invention at the same rolling temperatures.

Alloys contemplated herein are also characterized by good weldability. Excellent crack-free weld beads have been obtained in welding an alloy of the invention containing 50% nickel, 39% chromium, 2% titanium, 1% aluminum, balance iron by autogenous and matching filler weld techniques. An impact energy of 45.5 foot-pounds was obtained in testing a Charpy V-notch specimen from a plate of the alloy welded with matching filler metal. For obtaining a good combination of hardness and impact energy, it is advantageous to heat treat weldments by heating for 2 hours at 2200° F., air cool, and age for 2 hours at 1200° F. With such a treatment, a Rockwell C hardness of 41 and an impact energy of 20 foot-pounds were obtained.

Due to the high degree of hot plasticity of the fine grained alloys of the invention, articles thereof can be shaped by blow forming or by vacuum suction techniques. For example, a corrosion resistant, unfired pressure vessel can be produced by providing a tube of the fine grain gamma-alpha alloy, welding one end of the tube closed

gas-tight, heating a portion of the tube to about 1800° F., connecting the open end of the tube to a gas pressure source and expanding the heated portion to a predetermined size by fluid pressure exerted at the interior of the tube. Thereafter, the pressure is released, the article cooled to room temperature and the open end of the tube shortened to desired length. Another illustration is the production from a flat plate, of a dished, dimpled or grooved article, by a procedure wherein a heated portion of the plate is bulged and expanded by gas pressure on one side to force the opposite side into contact with an open-faced forming die.

The present invention is particularly applicable to the production of corrosion resistant nickel-chromium alloy products including sheet, strip, plate, bar, billets, rod, wire, etc., and to corrosion resistant nickel-chromium alloy articles, e.g., tubes, hypodermic needles, knives, surgical instruments, unfired pressure vessels, metal bottles, pans, dishes, containers, etc.

Very useful levels of strength are obtainable at moderately elevated temperatures up to about 600° F. or 800° F., or even 1000° F. For instance, alloy 39 of Tables VII and VIII when age hardened, had yield strengths of 226,500 p.s.i. at 600° F., 151,000 p.s.i. at 800° F. and 46,400 p.s.i. at 1000° F.

The invention is also applicable to the production of corrosion resistant nickel-chromium alloy articles and products by superplastic working processes such as stretching, piercing, fluid pressure forming methods including vacuum forming and positive pressure forming, punching, etc. Further, it is particularly noted that the new alloys hereof are also useful for cladding on other materials and in view of the excellent hot formability and high corrosion resistance of the alloy it is especially well suited for application on other materials to provide corrosion resistant coatings thereon by various known methods. The alloys made using magnesium, boron, calcium and/or zirconium (in addition to the alloys containing titanium) as provided by the invention are particularly useful for producing clad products and other products and articles made by processes of a compressive forming nature such as rolling, press forming, extruding, gas pressure bonding, hot pressing, etc.

While the present invention is described herein in connection with preferred methods of providing the required fine grain structure by hot working the alloy down through a temperature of alpha phase precipitation, e.g., hot forging a cast nickel-chromium alloy of composition in accordance with the invention from 2200° F. down through 1800° F., it is to be understood that the present invention also includes embodiments of the fine grain gamma-alpha phase alloy described herein when produced by other methods, e.g., powder metallurgical methods, available to those skilled in the art.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

We claim:

1. A fine grain, gamma-alpha phase wrought nickel-chromium alloy having a microstructure consisting essentially of fine gamma phase grains, chromium-rich alpha phase particles and optionally gamma prime phase in said gamma grains, with said fine gamma grains being of a gamma grain size less than 12 microns and with at least a portion of said chromium-rich alpha particles being not larger than 10 microns in average cross section size and disposed intergranularly at grain boundaries of the gamma phase grains, said wrought alloy being of a nickel-chromium alloy composition containing about 19% to about 60.5% nickel, up to about 10% cobalt substituted for an

equal percentage of nickel, up to about 55% iron, up to 0.1% carbon, up to about 2.76% of a plasticizer selected from the group consisting of up to about 2.5% titanium, up to about 0.1% magnesium, up to about 0.1% zirconium, up to about 0.05% calcium, up to about 0.015% boron and mixtures thereof, chromium in an amount effective to provide at least 2% of said chromium-rich alpha phase in excess of the solubility limit of said alpha phase in said gamma phase at 1800° F. and not greater than 55% chromium, provided the amount of chromium is not greater than the percentage determined by the relationship

$$\text{Percent Cr} = 68.9 - 0.435 (\text{percent Ni})$$

and further provided the total percentage of any elements other than nickel, cobalt, chromium, iron and plasticizer in the alloy is not greater than 7%, and characterized by the superplastic deformability characteristic of deformability to an elongation of at least 150% in tension at 1800° F. at a constant strain elongation rate from an initial strain rate of at least about 0.16 inch per inch per minute.

2. An alloy as set forth in claim 1 wherein the total percentage of any elements other than nickel, cobalt, chromium, iron and plasticizer in the alloy consists of up to 7% of elements from the group consisting of up to about 3% molybdenum and up to about 1.5% tungsten with the total of any molybdenum plus one-half the percentage of any tungsten not exceeding 3%, up to 1.5% aluminum provided that the total of any aluminum and any titanium in the alloy is not greater than 3.5%, up to about 2.5% columbium and up to about 4% tantalum with the total of any columbium plus one-half the percentage of any tantalum not exceeding about 2.5%, up to about 3% copper, up to about 1% beryllium, up to about 0.5% silicon, up to about 0.5% manganese, up to about 0.2% vanadium, up to about 0.1% carbon and mixtures thereof.

3. A process comprising plastically deforming a fine grain gamma-alpha phase wrought nickel-chromium alloy as set forth in claim 1 to a preselected shape at a temperature of about 1500° F. to 2000° F. while maintaining the alloy in a fine grain gamma alpha phase condition.

4. A process for imparting superplastic deformability at 1800° F. to a nickel-chromium alloy comprising providing an alloy consisting essentially of about 19% nickel to about 60.5% nickel, up to about 10% cobalt substituted for an equal percentage of nickel, up to 2.76% of plasticizer from the group consisting of up to about 2.5% titanium, up to about 0.1% magnesium, up to about 0.1% zirconium, up to about 0.05% calcium, up to about 0.015% boron and mixtures thereof, up to about 0.1% carbon, up to about 3% molybdenum and up to about 1.5% tungsten with the total of any molybdenum plus one-half the percentage of any tungsten not exceeding 3%, up to about 1.5% aluminum with the total of any aluminum and any titanium not exceeding 3.5%, up to about 2.5% columbium and up to about 4% tantalum with the total of any columbium plus one-half the percentage of any tantalum not exceeding about 2.5%, up to about 3% copper, up to about 1% beryllium, up to about 0.5% silicon, up to about 0.5% manganese, up to about 0.2% vanadium and containing chromium in an amount effective to provide at least 2% chromium-rich alpha phase in excess of the solubility limit of said alpha phase in said gamma phase at 1800° F. and not greater than 55% chromium, provided the percentage of chromium is not greater than the amount determined by the relationship

$$\text{Percent Cr} = 68.9 - 0.435 (\text{percent Ni})$$

and balance essentially iron with the proviso that the total percentage of any elements other than nickel, chromium, cobalt, iron and plasticizer is not greater than 7%, in a gamma phase solid solution condition containing precipitable alpha chromium, mechanically working and

recrystallizing the gamma phase to a fine gamma grain size less than 12 microns and precipitating fine alpha chromium particles of average cross section size not greater than 10 microns intergranularly adjacent to fine gamma grains while maintaining a fine gamma grain structure with a gamma grain size not greater than 12 microns, thereby imparting to the alloy a fine-grain gamma-alpha microstructure characterized by the superplastic deformability characteristic of deformability to an elongation of at least 150% in tension at 1800° F. at a constant elongation rate from an initial strain rate of at least about 0.16 inch per inch per minute.

5. An alloy as set forth in claim 1 in containing about 30% to 98% gamma phase and 2% to about 70% alpha phase.

6. An alloy as set forth in claim 1 containing about 30% to 90% gamma phase and 10% to 70% alpha phase.

7. An alloy as set forth in claim 1 wherein the gamma phase has an average grain size up to about 10 microns and the intergranularly dispersed alpha particles have an average cross section size up to about 10 microns.

8. An alloy as set forth in claim 1 wherein the average gamma grain size is up to about 3 microns.

9. An alloy as set forth in claim 1 containing at least 0.2% effective titanium.

10. An alloy as set forth in claim 1 containing at least 0.36% effective titanium and wherein the amount of chromium is not less than the percentage determined by the relationship

$$\text{Percent Cr} = 0.253 (\text{percent Ni}) + 22.9$$

when the nickel content is about 19% to about 53.5% and is not less than the percentage determined by the relationship

$$\text{Percent Cr} = 0.550 (\text{percent Ni}) + 7.0$$

when the nickel content is greater than 53.5% and up to 59.8%.

11. An alloy as set forth in claim 10 wherein the amount of chromium is not greater than the percentage determined by the relationship

$$\text{Percent Cr} = 0.361 (\text{percent Ni}) + 25.1$$

12. An alloy as set forth in claim 1 containing not more than 1% cobalt.

13. An alloy as set forth in claim 1 containing at least 7% iron.

14. An alloy as set forth in claim 1 containing 34% to about 43% chromium, about 7% to 34% iron, about 0.55% to 2.5% titanium, up to about 0.08% carbon, up to about 1.4% aluminum, with at least 0.36% effective titanium and a titanium-to-aluminum ratio of at least about 1.5:1 characterized by superplastic deformability enabling the alloy to be elongated at least 500% in tension at 1800° F. at a constant elongation rate from an initial strain rate of at least about 0.16 inch per inch per minute.

15. An alloy as set forth in claim 1 containing about 1% to 2% titanium, about 0.5% to 1.5% aluminum with the sum of the aluminum plus the titanium being about 2.5% to 3.5% and with not more than 30% iron, said alloy being characterized by superplastic deformability enabling the alloy to be elongated at least about 150% in tension at a constant elongation rate from an initial strain rate of at least about 0.16 inch per inch per minute at 1800° F. and being also characterized by ultimate tensile strength of at least about 200,000 pounds per square inch at room temperature when in the age hardened condition.

16. An alloy consisting essentially of about 19% to about 55.9% nickel, at least 0.2% effective titanium and up to about 2.5% titanium, up to about 0.1% carbon, chromium in an amount of at least about 24.5% and not greater than 43.1% provided the percent chromium

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is not less than the amount required to satisfy the relationship

$$\text{Percent Cr} = 0.253(\text{percent Ni}) + 22.9 - K(\text{percent eff. Ti} - 0.36)$$

when the nickel content is about 19% to about 53.5% and the percent chromium is not less than the amount required to satisfy the relationship

$$\text{Percent Cr} = 0.550(\text{percent Ni}) + 7.0 - K(\text{percent eff. Ti} - 0.36)$$

when the nickel content is greater than 53.5% and up to 55.9%, where K equals about 1.5 and "percent eff. Ti" is the percent titanium in the alloy reduced by about 4 times the percent carbon in the alloy but is not less than zero, and further provided the percent chromium is not greater than the amount determined by the relationship

$$\text{Percent Cr} = 0.361(\text{percent Ni}) + 25.1$$

up to about 10% cobalt substituted for an equal percentage of nickel, up to about 1.5% aluminum provided the sum of the percent aluminum plus the percent titanium does not exceed 3.5%, up to about 2.5% columbium and up to about 4% tantalum provided the sum of the percent columbium plus one-half the percent tantalum in the alloy does not exceed about 2.5%, up to about 3% molybdenum and up to about 1.5% tungsten provided the sum of the percent molybdenum plus one-half the percent tungsten does not exceed 3%, up to about 3% copper, up to about 1% beryllium, up to about 0.5% silicon, up to about 0.5% manganese, up to about 0.2% vanadium with the balance being essentially iron and with the iron content being at least 7% of the alloy and further provided that the total percentage of any elements other than nickel, titanium, chromium, cobalt and iron in the alloy is not greater than 7%.

17. An alloy as set forth in claim 16 containing at least about 0.36% effective titanium.

18. An alloy as set forth in claim 16 containing at least 0.36% effective titanium and wherein the amount of chromium is not less than the percentage determined by the relationship

$$\text{Percent Cr} = 0.253(\text{percent Ni}) + 22.9$$

when the nickel content is about 19% to about 53.5% and is not less than the percentage determined by the relationship

$$\text{Percent Cr} = 0.550(\text{percent Ni}) + 7.0$$

when the nickel content is greater than 53.5%.

19. An alloy as set forth in claim 16 containing 34% to about 43% chromium, about 7% to 34% iron, about 0.55% to 2.5% titanium, up to about 0.08% carbon, up to about 1.4% aluminum, with at least 0.36% effective titanium and a titanium-to-aluminum ratio of at least about 1.5:1, said alloy being characterized by good cold workability at room temperature in the gamma-phase solid solution condition and by superplastic deformability at 1800° F. to an elongation of at least 500% in tension at a constant strain elongation rate from an initial strain rate of at least about 0.16 inch per inch per minute in the fine-grain gamma-alpha phase condition having an average grain size not greater than 3 microns.

20. A process as set forth in claim 4 wherein at least

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2% of fine particles of chromium-rich alpha phase is precipitated intergranularly at grain boundaries of the gamma grains and at least about 30% of the alloy is retained as gamma phase.

21. A process as set forth in claim 4 wherein the chromium content of the nickel-chromium alloy is not greater than the amount determined by the relationship

$$\text{Percent Cr} = 0.361(\text{percent Ni}) + 25.1$$

and the alloy is cold worked in a substantially all-gamma phase condition with precipitable alpha chromium dissolved therein and is thereafter heated to at least the recrystallization temperature of said cold worked alloy to thereby recrystallize said cold worked alloy to a fine grain condition having fine gamma grains of average particle size not greater than 10 microns and to precipitate fine particles of chromium-rich alpha phase intergranularly adjacent to grain boundaries of the gamma grains.

22. A process as set forth in claim 4 wherein the nickel-chromium alloy having precipitable chromium dissolved in the alloy matrix is hot worked while precipitating alpha chromium.

23. A process as set forth in claim 22 wherein the chromium content of the nickel-chromium alloy is not greater than the amount determined by the relationship

$$\text{Percent Cr} = 0.361(\text{percent Ni}) + 25.1$$

and the alloy is in a substantially all-gamma phase condition with precipitable alpha chromium dissolved therein at the initiation of the hot working prior to precipitation of alpha chromium.

24. A process as set forth in claim 3 wherein the alloy is extended in tension at 1800° F. to elongate the alloy at least 150%.

25. A process as set forth in claim 3 wherein the alloy is stressed in tension while being plastically deformed to the preselected shape by forcing the alloy against a forming die.

26. A process as set forth in claim 25 wherein deforming force is applied by fluid pressure.

27. A process as set forth in claim 3 wherein the heated alloy is in the form of a hollow body and is stretched in tension by applying fluid pressure to an interior surface of the hollow body.

28. A process as set forth in claim 3 wherein the nickel-chromium alloy is formed as a cladding on a second material having a surface with the preselected shape by forcing the nickel-chromium alloy into continuous contact with the surface of said second material having the preselected shape.

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72—364, 377 75—128, 176; 148—12.3, 12.7, 31, 32.5

UNITED STATES PATENT OFFICE CERTIFICATE OF CORRECTION

Patent No. 3,519,419

Dated July 7, 1970

Inventor(s) ROBERT CAMERON GIBSON, HOWARD WAYNE HAYDEN, JR.
JOHN RAYMOND MIHALISIN & JERE HALL BROPHY

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 22, for "relationship." read
--relationships.--.

Column 5, line 21, for "dameters" read --diameters--;
line 56, for "or" read --of--.

Column 6, lines 17 and 18, for "Ni₃ Ti, Al)" read
--Ni₃ (Ti, Al)--.

Column 7, line 41, for "metallurfical" read
--Metallurgical--; line 54, for "all-gramma" read --all-gamma--;
and line 74, insert --about-- before "3%".

Column 9, line 45, for "Extursion" read --Extrusion--.

Column 10, line 9, for "srength" read --strength--.

Column 12, line 49, insert --are-- before "thus".

Column 15, Table VII, per cent aluminum for Alloy No. 39,
for "1.05" read --1.18--.

Column 16, lines 10 to 16, last column of Table IX for

<u>"Elong- gation</u>	<u>read --Elong- gation</u>
101	100
00	20
120	120
120	100
04	64
60	80
186	116
--"	-- --.

Signed and sealed this 15th day of June 1971.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents